



(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
06.03.1996 Bulletin 1996/10

(51) Int Cl.⁶: C08F 265/02, C04B 24/26
// (C08F265/06, 2:22)

(21) Application number: 92306097.4

(22) Date of filing: 01.07.1992

(54) Process for the preparation of a redispersible core-shell polymer

Verfahren zur Herstellung eines redispersierbaren Kern-Schale-Polymer

Procédé de préparation d'un polymère coeur-enveloppe redispersable

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU MC NL
PT SE

(30) Priority: 11.07.1991 US 728398

(43) Date of publication of application:
13.01.1993 Bulletin 1993/02

(73) Proprietor: ROHM AND HAAS COMPANY
Philadelphia Pennsylvania 19105 (US)

(72) Inventors:

- Tsai, Min-Chi
Ambler, PA 19002 (US)
- Papsin, George Arthur, Jr.
North Wales, PA 19454 (US)
- Chlou, Shang-Jaw
Lower Gwynedd, PA 19002 (US)

(74) Representative: Angell, David Whilton et al
ROHM AND HAAS
European Operations Patent Department
Lennig House
2 Mason's Avenue
Croydon CR9 3NB (GB)

(56) References cited:
EP-A- 0 338 486 EP-A- 0 338 486
EP-A- 0 348 565 US-A- 4 876 313

- CHEMICAL ABSTRACTS, vol. 89, no. 18, 1
October 1978, Columbus, Ohio, US;
- abstract no. 147389E, YAMAZAKI:
'manufacture of polymers by emulsion
polymerization' page 12 ;column 1 ;
- CHEMICAL ABSTRACTS, vol. 90, no. 10, 1
March 1979, Columbus, Ohio, US; abstract no.
73018E, UGAI ET AL.: 'adhesive compositions'
page 44 ;column 1 ;
- CHEMICAL ABSTRACTS, vol. 86, no. 4, 24
January 1977, Columbus, Ohio, US; abstract
no. 18513E, MATSUMOTO ET AL.:
'WATER-THINNED RESIN COATING
COMPOSITIONS' page 108 ;column 1 ;
- CHEMICAL ABSTRACTS, vol. 91, no. 22, 1
November 1979, Columbus, Ohio, US; abstract
no. 180324U, HIGASHI ET AL.: 'SYNTHETIC
RESIN EMULSION FOR CEMENT' page 315
;column 2 ;

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

The present invention relates to a process for the preparation of a redispersible core-shell polymer, preferably in the form of a powder.

5 In particular, the present invention relates to a process for the preparation of a core-shell polymer powder comprising a two-stage aqueous emulsion sequential process. The core-shell polymer powder is particularly useful as an acrylic modifier for cement. Also, the core-shell polymer powders of this invention have excellent physical properties such as redispersability and, when used as a cement modifier, provide excellent properties in thin section application, provide

10 The use of redispersible polymer powders as cement modifiers is known. However, in order for the polymer powder to be effective, the following critical requirements have to be met: it should be capable of flowing freely, it should have a long storage life and it should be redispersible in water. Additionally, the polymer powders should be suitable in shear-bond adhesion applications and should have superior properties when the powder is used to modify thin sections of cement. These properties are fulfilled only partially by powders which are prepared utilizing prior art blends, mixtures

15 and core-shell polymer processes. Mixtures and blends of soluble resins with insoluble emulsion polymers are known in the art and are generally used both alone and in various formulations as coatings and impregnates for cementitious applications. The soluble resin is generally prepared by solution polymerization, such as described in US-A-3,037,942.

20 It is also known that core-shell emulsion polymers made significant improvements over prior art mixtures and blends such as described in US-A-4,916,171. By polymerizing one component in the presence of the other to form a core-shell emulsion polymer, improvements in stability, rheology and water resistance were realized. It is still further known that the addition of an emulsion acrylic polymer as a powder dispersion in cementitious mixtures improves properties such as adhesion and strength of the cement matrix. For example, latex modified Portland cement is a premixed material wherein a polymer is added to the fresh concrete mixture in a liquid, powder or dispersed phase and cured. However,

25 while the addition of core-shell emulsion polymers have improved some properties of premixed cement, other deficiencies still remain such as, for example, stability and redispersability of the acrylic emulsion. US-A-4,151,143 (Blank, et al.) claims a surfactant-free emulsion polymer coating composition and method for preparing the same. Blank, et al. discloses that the presence of surfactants is a significant problem with emulsion polymers employed as coatings. Surfactants are required to stabilize emulsion polymers; however, the presence of surfactants

30 adversely affect the water and corrosion resistance of the resulting film as well as the adhesion of the coating to metal substrates. Blank, et al. emulsion polymers are prepared in a two-stage process. The process includes (1) a first stage wherein a carboxyl group containing polymer is prepared by a conventional solution or bulk polymerization technique and then water-dispersed or solubilized by partial or full neutralization with an organic amine or base and high shear agitation,

35 and (2) a second stage wherein a mixture of polymerizable monomers and polymerization catalyst is added to the first-stage emulsion at an elevated temperature to affect polymerization of the stage two monomers resulting in the formation of an emulsion coating composition. The coating composition is alleged to be surfactant-free. Two-stage emulsion polymers are known to exist in many morphological forms which are determined by many factors including the relative hydrophilicity, miscibility and molecular weights of the first- and second-stage polymers.

40 So-called "core-shell" polymers are formed when the second-stage polymers form a "shell" or coating around a discrete domain or "core" of the first-stage polymer. Examples of such core-shell polymers are disclosed in US-A-4,916,171. Also, US-A-4,876,313 discloses the use of polyfunctional compounds to chemically graft or bond the shell to the core in order to improve the resulting film's properties such as stability, water resistance and rheology after the addition of formulation additives, such as alcohol.

45 "Inverse core-shell" emulsion polymers, such as disclosed in US-A-4,876,313, are also known. Inverse core-shell polymers are those where the second-stage polymer becomes the core and is surrounded by the shell which, in the inverse process, is the first-stage polymer.

These inverse compositions can be formed when the first-stage polymer is more hydrophilic than the second-stage monomer (Lee and Ishikawa, *The Formation of Inverted Core-Shell Latexes*, *J. Poly. Sci.*, vol. 21, pages 147-154 (1983)).

50 While core-shell polymers have made significant improvements in such polymer properties such as chemical and water resistance, stability and rheology, additional improvements are required. Therefore, in order for the core-shell polymers to be especially useful in cementitious formulations: it must possess the desired morphology; it must be stable; it must be compatible with cement; it must possess bulk mortar curing capability without significantly retarding the curing process; and, it must demonstrate excellent toughness and adhesion, especially when applied in thin sections.

55 What is required is a novel generation of core-shell polymer powders that are easily redispersible, stable, and that do not significantly retard mortar curing, while maintaining other properties such as shear bond adhesion, strength and trowelability.

The present invention seeks to overcome the problems associated with the known processes and polymers.

According to a first aspect of the present invention there is provided a two-stage aqueous emulsion sequential polymerization method for the preparation of a core-shell polymer, preferably in the form of a powder, comprising: i. in a first stage (a) forming a mixture of monomers comprising from 5 to 40 percent of a carboxylic acid or anhydride, and from 30 to 95 percent of an alkyl acrylate or alkyl methacrylate or styrene, from 0 to 30 percent of a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide, (b) polymerizing the mixture in the presence of a polyfunctional compound to form a shell polymer, (c) neutralizing the shell with an amine or a base; and ii. in a second stage, (d) forming a mixture of monomers comprising from 70 to 100 percent of an alkyl acrylate or methacrylate or styrene and from 0 to 30 percent of a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide to produce a calculated Tg of -65 to +35°C; iii. combining the second-stage monomers mixture with the neutralized polymer of the first stage; iv. polymerizing the combined monomers of the second stage to form the aqueous emulsion core-shell polymer; and, optionally v. converting the aqueous emulsion core-shell polymer by spray-drying into a redispersable polymer powder.

According to a second aspect of the present invention there is provided a core-shell polymer obtainable by the first aspect of the present invention.

According to a third aspect of the present invention there is provided a core-shell polymer obtainable or obtained by the first aspect of the present invention admixed with an effective amount of Portland cement.

According to a fourth aspect of the present invention there is provided a method of modifying cementitious compositions comprising admixing an effective amount of Portland cement with an effective amount of the core-shell polymer, preferably in the form of a powder, obtainable or obtained by the first aspect of the present invention.

The advantages associated with the present invention are that it provides core-shell emulsion polymers that are shelf-stable, compatible with cement, allows bulk mortar curing and have excellent toughness and adhesion. Also, it provides grafted core-shell polymers by a two-stage process employing polyfunctional compositions. Also, it provides core-shell polymers that promote superior application properties such as adhesion and toughness when employed in cement formulations. Also, it provides core-shell polymers that are stable during spray drying. Also, it provides redispersible and storage stable core-shell polymer powders that perform in the application step. Also, it provides core-shell polymers with unique economic advantages during spray dry processing.

The core-shell polymer powders of this invention have excellent physical properties such as redispersability and, when used as a cement modifier, provide excellent properties in thin section application, provide adhesion to a variety of substrates and provide tensile, flexural and compressive strength.

Preferably, the weight ratio of the core to the shell is from 95:05 to 60:40, the core having an average molecular weight of greater than 100,000 and the shell having an average molecular weight of 2,500 to 12,000 for the hydrolyzed shell, as determined by gel permeation chromatography.

Preferably, the Tg of the shell is greater than 60°C, preferably greater than 80°C, and the Tg of the core is from -65 to +35°C, preferably from -40 to +25°C.

Preferably, the mixture of monomers comprising the shell and the core are selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, butyl methacrylate, acrylonitrile, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylic anhydride, methacrylic anhydride, maleic anhydride, itaconic anhydride, fumaric anhydride, styrene, substituted styrene, vinyl acetate and other C₁ to C₁₂ alkyl acrylates and methacrylates, acrylamide, methacrylamide, N-methylol methacrylamide, and N-methylol acrylamide.

Preferably, the mixture of monomers comprising the shell are 5 to 40 percent of a carboxylic acid or anhydride and from 60 to 95 percent of an alkyl acrylate or alkyl methacrylate or styrene, based on the total weight of the shell.

Preferably, the mixture of monomers comprising the shell are methyl methacrylate, and methacrylic acid.

Preferably, the mixture of monomers comprising the shell have been neutralized with a base selected from the group consisting of ammonia, triethylamine, monoethanolamine, dimethylaminoethanol, sodium hydroxide and calcium hydroxide and all other Group I A and II A hydroxides. Preferably, the base is a blend of 30 - 60% calcium hydroxide and 40 - 70% sodium hydroxide, preferably 35 - 50% calcium hydroxide and 50 - 65% sodium hydroxide, based on the total equivalents of acid neutralized. Preferably, the base is 100 percent ammonia.

Preferably, the mixture of monomers comprising the core are 0 to 5 percent of a carboxylic acid or anhydride or acrylamide and from 95 to 100 percent of an alkyl acrylate or alkyl methacrylate or styrene, based on the total weight of the core.

Preferably, the mixture of monomers comprising the core are butyl acrylate and methyl methacrylate.

Preferably, the mixture of monomers comprising the core are butyl acrylate and styrene.

Preferably, the polyfunctional compound is selected from the group consisting of polyfunctional compounds having two or more sites of unsaturation, reactive chain transfer agents having two or more abstractable atoms and hybrid polyfunctional compounds having one or more sites of unsaturation and one or more abstractable atoms.

Preferably, the polyfunctional compound is allyl methacrylate.

Preferably, the polyfunctional compound comprises from less than about 5 percent, preferably from 0.5 to 3.0 percent

based on the total weight of the shell.

Preferably, the polymer is admixed with an effective amount of Portland cement.

The present invention therefore provides a process for the preparation of a stable, easily redispersible core-shell polymer powder prepared from spray drying a latex polymer. The latex polymer is produced by a two-stage sequential process: by forming an aqueous-insoluble polymer core with an alkali-soluble polymer shell, wherein the alkali-soluble shell polymer is polymerized in the presence of a polyfunctional compound from a mixture of monomers which have acid functionality, the shell polymer is then neutralized with a base or an amine and, in a subsequent polymerization step, a mixture of monomers is polymerized in the presence of the previously neutralized shell polymer to form an aqueous-insoluble core polymer.

The core and the shell components are chemically grafted together by carrying out the emulsion polymerization of the core in the presence of at least one polyfunctional compound which is present in the shell monomers.

The present invention therefore relates to core-shell polymers produced by a two-stage aqueous emulsion sequential process and their subsequent use as a solid modifier for cementitious materials. By utilizing the process of this invention, a core-shell emulsion polymer product is produced where the core-shell polymers have an aqueous-insoluble polymer core and an alkali-soluble polymer shell, wherein the core and shell are chemically grafted together to a significant or substantial extent such that the core and shell are permanently attached.

The compositions of the invention comprise grafted core-shell polymers such that, upon dissolving the shell with alkali, a significant portion of the shell remains permanently attached to the core. It is this permanent attachment of the shell and core through chemical grafting which is believed to provide stability to the core-shell polymer and physical properties to the cementitious mixtures that were previously unrealized using prior core-shell processes as well as processes involving polymer blends and polymer mixtures.

Typically, there are two techniques for preparing the grafted core-shell polymers.

Technique (1) is an emulsion polymerization of a mixture of monomers comprising a carboxylic acid or anhydride and an alkyl acrylate or alkyl methacrylate or styrene or substituted styrene, acrylamide or methacrylate or hydroxyalkyl ester of a carboxylic acid in the presence of a polyfunctional monomer to form a shell polymer, neutralizing the previously formed shell with an amine or base and, in a second stage, forming a mixture of monomers comprising an alkyl acrylate or methacrylate, styrene or substituted styrene and a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide, methylolated acrylamide or methacrylamide, combining the second-stage monomers with the first stage and polymerizing the mixture to form the core-shell polymers of this invention.

Technique (2), which is a method according to US-A-4,916,171, is an emulsion polymerization of a mixture of monomers comprising an alkyl acrylate or methacrylate and a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide in the presence of a polyfunctional monomer to form a core polymer and, in a second stage, forming a mixture of monomers comprising a carboxylic acid or anhydride and an alkyl acrylate or alkyl methacrylate, combining the second-stage monomers with the first stage and polymerizing the mixture to form the core-shell polymers.

Suitable monofunctional monomers for the preparation of the core and the shell polymers are selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, butyl methacrylate, acrylonitrile, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylic anhydride, methacrylic anhydride, methylolated acrylamide and methyl methacrylamide, methacrylamide, acrylamide, divinyl benzene, half esters of maleic anhydride / fumaric / itaconic, maleic anhydride, itaconic anhydride, fumaric anhydride, styrene, substituted styrene, vinyl acetate and other C₁ to C₁₂ alkyl acrylates and methacrylates.

The weight ratio of the core polymer to the shell polymer is preferably 95:05 to 60:40, more preferably 90:10 to 70:30, and most preferably 85:15 to 75:25. Preferably, the core polymer has a weight average molecular weight greater than 100,000, and the shell polymer has a weight average molecular weight of 2,500 to 12,000 as determined by aqueous gel permeation chromatography on the hydrolyzed sample. Preferably, the glass transition temperature (T_g) calculated by the "Fox Equation" of the core polymer is -65°C to 35°C, and the T_g of the shell is greater than 60°C.

The polyfunctional compounds useful in chemically grafting the core and shell together are selected from (a) polyfunctional compounds having two or more sites of unsaturation, (b) reactive chain transfer agents having two or more abstractable atoms, and (c) hybrid polyfunctional compounds having one or more sites of unsaturation and one or more abstractable atoms. However, compounds such as the glycidyl-containing vinyl monomers and vinyl isocyanates described in US-A-4,565,839, are not suitable as polyfunctional compounds for this invention because they do not work to graft the core to the shell in aqueous-based emulsion polymerizations.

The polyfunctional compounds useful in the two-stage process of this invention are selected from the group consisting of allyl-, methallyl-, vinyl-, dicylopentenyl and crotyl-esters of acrylic, methacrylic, maleic (mono- and di-esters), fumaric (mono- and di-esters) and itaconic (mono- and di-esters) acids; allyl-, methallyl-, and crotyl-vinyl ether and thioether; N- and N,N-di-allyl-, methallyl-, crotyl-, and vinyl-amides of acrylic and methacrylic acids; N-allyl-, methallyl-, and crotyl-maleimide; vinyl esters of 3-butenic and 4-pentenoic acids; diallyl phthalate; triallyl cyanurate; O-allyl-, methallyl-crotyl-, O-alkyl-, aryl-, P-vinyl-P-allyl-, P-crotyl-, and P-methallyl-phosphonates; triallyl-, trimethallyl-, and tricro-

tyl-phosphates; O-vinyl-, O,O-diallyl-, dimethallyl-, and dicrotyl-phosphates; alkenyl and cycloalkenyl esters of acrylic, methacrylic, maleic (mono- and di-esters), fumaric (mono- and di-esters), and itaconic (mono- and di-esters) acids; vinyl ethers and vinyl thioethers of cycloalkenols and cycloalkene thiols; vinyl esters of cycloalkene carboxylic acids; conjugated dienes such as 1,3-butadiene, and isoprene; paramethylstyrene; chloromethylstyrene; allyl-, methallyl-, and crotyl-mercaptan; bromotrichloromethane; bromoform; carbon tetrachloride; and carbon tetrabromide.

Additionally, the polyfunctional compound can be selected from the group consisting of ethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, polyethyleneglycol dimethacrylate, polypropyleneglycol dimethacrylate, neopentylglycol dimethacrylate, 1,3-butyleneglycol diacrylate, neopentylglycol diacrylate, trimethylolethane trimethacrylate, dipentaerythritol triacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, 1,3-butyleneglycol dimethacrylate, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, tripropyleneglycol diacrylate, and divinyl benzene.

Preferred polyfunctional compounds suitable for use in this invention may be selected from the group consisting of allyl-, methallyl-, dicyclopentenyl-, crotyl- and vinyl-esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters), fumaric acid (mono- and di-esters) and itaconic acid (mono- and di-esters); N- or N,N-di-, methallyl-, crotyl- and vinyl-amides of acrylic acid and methacrylic acid; N-methallyl and crotyl-maleimide; alkenyl or cycloalkenyl esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters), fumaric acid (mono- and di-esters), fumaric acid (mono- and di-esters), itaconic acid (mono- and di-esters); 1,3-butadiene; isoprene; divinyl benzene; methallyl-, crotyl- and allyl-mercaptan.

Preferably, the polyfunctional compound(s) should be present in an amount less than 5 percent by weight of the shell, more preferably 0.5 to 3.0 percent of the shell. The most preferred polyfunctional compound is allyl methacrylate.

Suitable monomers for use in preparing the shell monomer of this invention include those listed above for the preparation of the core. However, it is critical to the preparation of core-shell polymers of this invention that higher levels of acid-containing monomers are used in the shell than in the core in order to induce alkali solubility.

The shell polymer, referred to hereinafter also as the "first stage", is formed from a mixture of monomers comprising from 5 to 40 percent by weight of a carboxylic acid or anhydride, and from 30 to 95 percent of an alkyl acrylate or alkyl methacrylate or styrene, and from 0 to 30 percent of a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide. Preferred levels of acid-containing monomer(s) for the shell range from 15 to 35 percent by weight of the shell polymer. The most preferred acid-containing monomers for use in preparing the shell polymer is methacrylic acid. Anhydrides, such as methacrylic anhydride, maleic anhydride, and itaconic anhydride, may be used in place of the acid-containing monomers in the shell polymer.

Preferably, the shell polymer comprises 95 to 60 percent by weight methyl methacrylate. The shell polymer preferably has a weight average molecular weight of 2,500 to 12,000 as determined by gel permeation chromatography.

Common chain transfer agents or mixtures thereof known in the art, such as alkylmercaptans, are employed to control molecular weight, preferably C₁ - C₆ alkyl and alkyloxy mercaptans.

Based on equivalents of acid in the shell polymer, 0.8 to 1.5 equivalents of base are added to the shell, and more preferably .95 to 1.10 equivalents of base are added to the shell polymer compositions to neutralize and substantially, but not necessarily totally, dissolve the shell polymer so as to form a neutralized shell polymer and an aqueous solution of neutralized shell polymer. Polymerization of the core in the presence of the neutralized shell results in some of the shell polymer remaining permanently attached to the core. Bases that are suitable for use in this invention can be any kind of base, but is preferably selected from the group consisting of ammonia, triethylamine, monoethanolamine, dimethylaminoethanol, sodium hydroxide and calcium hydroxide and all other Group I A and II A hydroxides.

The core-shell polymers of this invention are particularly useful as dry modifiers for cement mortars.

The polymers are easily isolatable by conventional methods such as spray drying to yield dry, free-flowing powders which, upon admixture with cementitious compositions, provide superior physical properties and performance characteristics.

The present invention will now be described by way of examples only.

In the following examples the following abbreviations will be used.

Sodium Lauryl Sulfate (SLS)

Butyl Acrylate (BA)

Methyl Methacrylate (MMA)

Methacrylic Acid (MAA)

Allyl Methacrylate (ALMA)

Methyl-3-Mercaptopropionate (MMP)

Ammonium Persulfate (APS)

t-Butyl Hydroperoxide (t-BHP)

Sodium Sulfoxylate Formaldehyde (SSF)

Hydroxy Ethyl Methacrylate (HEMA)

Crotyl Methacrylate (CMA)
 Styrene (STY)
 Acrylamide (AM)
 Ethylene-Vinyl Acetate (EVA)

5

PREPARATIONS

Example 1 - Two-Stage Sequential Core-Shell Polymer Process: Shell Levels

10 Example 1(a) - 10% Shell

800 g of DI water was charged to a 5 liter, 4-necked round bottom flask equipped with a mechanical stirrer, condenser and appropriate fittings to produce a nitrogen blanket over the reaction mixture. A monomer emulsion (ME #1) was then charged to the kettle followed by an initiator. A few minutes after the temperature leveled off, an NH_3 neutralizer was added which solubilized the polymer. The reactor contents were then heated to 85°C via a heating mantle and a second monomer emulsion (ME #2) was then gradually added to the same kettle containing the solubilized polymer at a rate so that the reaction temperature stayed in the neighborhood of 80°C to 85°C. The kettle contents were then cooled to 55°C and additional initiator was added to reduce residual monomers to low levels.

20

Material	ME #1	ME #2
DI H ₂ O	49.4	536
Pluronic L31 (L31)	---	---
58% Alipal CO-436	6.8	---
28% Sodium Lauryl Sulfate (SLS)	---	---
70% Triton X-165	---	50.6
Butyl Acrylate (BA)	---	885.7
Methyl Methacrylate (MMA)	154.4	859
Methacrylic Acid (MAA)	39.4	26.6
Allyl Methacrylate (ALMA)	3	---
Methyl 3-Mercaptopropionate (MMP)	6.9	---
Rinse DI H ₂ O	55	90
	315	2448

35

[Pluronic is a trade mark of BASF; Alipal is a trade mark of Rhone-Poulenc; Triton is a trade mark of Union Carbide.]

ME #1 Initiator

40

4.5 g of 0.1% Solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (keep acid with H_2SO_4).
 2.8 g of 70% t-Butyl Hydroperoxide (t-BHP) in 15 g of DI H₂O.
 2.9 g of Sodium Sulfoxylate Formaldehyde (SSF) in 35 g of DI H₂O.

Neutralizer

45

28 g of NH_3 in 28 g of DI H₂O.

ME #2 Initiator

50

3.3 g of Ammonium Persulfate (APS) in 200 g DI H₂O for the kettle charge and 3.0 g of APS in 114 g DI H₂O for a cofeed.

Final Polymer Characterization

55

Percent Solids: 48.5
 Particle Size (Brookhaven BI-90): 221 nm

EP 0 522 791 B1

pH: 6.8
Viscosity: 25 cps
Gel: Trace

5 Example 1(b) - 20% Shell

Use same procedure and recipe for example 1(a) except for: 1300 g of DI H₂O in the kettle and

Material	ME #1	ME #2
DI H ₂ O	100	395
Pluronic L31 (L31)	37.4	11.8
58% Alipal CO-436	1.4	---
28% Sodium Lauryl Sulfate (SLS)	---	11.2
70% Triton X-165	---	---
Butyl Acrylate (BA)	---	787.3
Methyl Methacrylate (MMA)	309	763.6
Methacrylic Acid (MAA)	78.7	23.6
Allyl Methacrylate (ALMA)	5.9	---
Methyl 3-Mercaptopropionate (MMP)	13.8	---
Rinse DI H ₂ O	100	90
	<u>646</u>	<u>2082.5</u>

25 [Pluronic is a trade mark of BASF; Alipal is a trade mark of Rhone-Poulenc; Triton is a trade mark of Union Carbide.]

ME #1 Initiator

30 10 g of 0.1% Solution of FeSO₄·7H₂O (keep acid with H₂SO₄).
5.6 g of 70% t-Butyl Hydroperoxide (t-BHP) in 25 g of DI H₂O.
5.8 g of Sodium Sulfoxylate Formaldehyde (SSF) in 55 g of DI H₂O.

35 Neutralizer

55 g of NH₃ in 55 g of DI H₂O..

ME #2 Initiator

40 2.6 g of Ammonium Persulfate (APS) in 200 g DI H₂O for the kettle charge and 2.6 g of APS in 115 g DI H₂O for a cofeed.

Final Polymer Characterization

45 Percent Solids: 43.4
Particle Size (Brookhaven BI-90): 110 nm
pH: 7.0
Viscosity: 25 cps
Gel: 4.5 g

55 Example 1(c) - 30% Shell

9.8 g of Borax in 1304 g of DI Water was charged to a 5 liter, 4-necked round bottom flask equipped with a mechanical stirrer, condenser and appropriate fittings to produce a nitrogen blanket over the reaction mixture. A monomer emulsion (ME #1) was then charged to the kettle followed by an initiator which produced a temperature exotherm. The reactor

EP 0 522 791 B1

contents were then heated to 65°C via a heating mantle and a second monomer emulsion (ME #2) was then gradually added to the same kettle containing the solubilized polymer at a rate so that the reaction temperature stayed in the neighborhood of 80 to 85°C. The kettle contents were then cooled to 55°C and additional initiator was added to reduce residual monomers to low levels.

Material	ME #1	ME #2
DI H ₂ O	150	306
34% Aerosol A103 (A103)	52.1	
28% Sodium Lauryl Sulfate (SLS)		38.1
Butyl Acrylate (BA)	---	688.8
Methyl Methacrylate (MMA)	374.5	668.2
Hydroxy Ethyl Methacrylate (HEMA)	59	
Methacrylic Acid (MAA)	118.1	20.7
Allyl Methacrylate (ALMA)	8.9	---
Methyl-3-Mercaptopropionate (MMP)	20.7	---
Rinse DI H ₂ O	100	75
	913.2	1797

[Aerosol is a trade mark of American Cyanamid]

ME #1 Initiator

24 g of 0.1% Solution of FeSO₄ 7H₂O (keep acid with H₂SO₄), 8.4 g of 70% t-Butyl Hydroperoxide (t-BHP) in 35 g of DI H₂O. 8.8 g of Sodium Sulfoxylate Formaldehyde (SSF) in 65 g of DI H₂O.

ME #2 Initiator

3.3 g of Ammonium Persulfate (APS) in 50 g DI H₂O for the kettle charge and 2.3 g of APS in 115 g DI H₂O for a cofeed.

Final Polymer Characterization

Percent Solids: 46.5
Particle Size (Brookhaven BI-90): 242 nm
pH: 5.7
Viscosity: 15 cps
Gel: trace

Example 1(d) - 30% Shell

Use same procedure and recipe for example 1(a) except for 1300 g of DI H₂O in the kettle and

Material	ME #1	ME #2
DI H ₂ O	150	346
Pluronic L31 (L31)	38.9	10.3
58% Alpal CO-436	2.0	---
28% Sodium Lauryl Sulfate (SLS)	---	9.8
Butyl Acrylate (BA)	---	688.8
Methyl Methacrylate (MMA)	442.7	668.2
Methacrylic Acid (MAA)	118.1	20.7
Allyl Methacrylate (ALMA)	8.7	---

Continuation of the Table on the next page

EP 0 522 791 B1

(continued)

Material	ME #1	ME #2
Methyl-3-Mercaptopropionate (MMP)	20.7	---
Rinse DI H ₂ O	100	90
	<u>881</u>	<u>1834</u>

[Pluronic is a trade mark of BASF; Alipal is a trade mark of Rhone Poulenc]

ME #1 Initiator

10 g of 0.1% Solution of FeSO₄·7H₂O (keep acid with H₂SO₄).
 8.4 g of 70% t-Butyl Hydroperoxide (t-BHP) in 35 g of DI H₂O.
 8.8 g of Sodium Sulfoxylate Formaldehyde (SSF) in 65 g of DI H₂O.

Neutralizer

82.1 g of NH₃ in 82.1 g of DI H₂O.

ME #2 Initiator

2.6 g of Ammonium Persulfate (APS) in 200 g DI H₂O for the kettle charge and 2.3 g of APS in 115 g DI H₂O for a cofeed.

Final Polymer Characterization

Percent Solids: 42.8
 Particle Size (Brookhaven BI-90): 120 nm
 pH: 7.3
 Viscosity: 35 cps
 Gel: 3.1 g

Example 2 - Two-Stage Sequential Core-Shell Polymer Process: Grafting

Comparative Example 2(a) - 0% ALMA

Use same procedure and recipe for example 1(a) except for: 1000 g of DI H₂O in the kettle and

Material	ME #1	ME #2
DI H ₂ O	98.8	477
Pluronic L31 (L31)	---	---
58% Alipal CO-436	6.8	---
28% Sodium Lauryl Sulfate (SLS)	---	---
Triton X-165	---	45.0
Butyl Acrylate (BA)	---	787.3
Methyl Methacrylate (MMA)	314.9	763.6
Methacrylic Acid (MAA)	78.7	23.6
Allyl Methacrylate (ALMA)	---	---
Methyl-3-Mercaptopropionate (MMP)	13.8	---
Rinse DI H ₂ O	55	90
	<u>568</u>	<u>2187</u>

EP 0 522 791 B1

[Pluronic is a trade mark of BASF; Alipal is a trade mark of Rhone-Poulenc; Triton is a trade mark of Union Carbide.]

ME #1 Initiator

5

4.5 g of 0.1% Solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (keep acid with H_2SO_4).
5.6 g of 70% t-Butyl Hydroperoxide (t-BHP) in 30 g of DI H_2O .
5.8 g of Sodium Sulfoxylate Formaldehyde (SSF) in 70 g of DI H_2O .

10

Neutralizer

56 g of NH_3 in 56 g of DI H_2O .

15

ME #2 Initiator

3.3 g of Ammonium Persulfate (APS) in 200 g DI H_2O for the kettle charge and 2.6 g of APS in 98.5 g DI H_2O for a cofeed.

20

Final Polymer Characterization

25

Percent Solids: 50.5
Particle Size (Brookhaven BI-90): 140 nm
pH: 7.1
Viscosity: 145 cps
Gel: 1 g

30

Example 2(b) - 1% ALMA

885 g of DI water was charged to a 5 liter, 4-necked round bottom flask equipped with a mechanical stirrer, condenser and appropriate fittings to produce a nitrogen blanket over the reaction mixture. The kettle contents were then heated to 75°C. A monomer emulsion (ME #1) was then charged to the kettle followed by an initiator. A few minutes after the temperature leveled off, a neutralizer was added which solubilized the polymer. Approximately 120 g of ME #2 was then added to the kettle followed by an APS initiator charge. The balance of the ME #2 was then gradually added to the same kettle containing the solubilized polymer at a rate so that the reaction temperature stayed in the neighborhood of 80°C to 85°C. The kettle contents were then cooled to 55°C and additional initiator was added to reduce residual monomers to low levels.

40

<u>Material</u>	<u>ME #1</u>	<u>ME #2</u>
DI H_2O	100	395
Pluronic L31 (L31)	37.4	11.8
58% Alipal CO-436	1.4	—
28% Sodium Lauryl Sulfate (SLS)	—	11.2
Butyl Acrylate (BA)	—	799.4
Methyl Methacrylate (MMA)	311	775.2
Methacrylic Acid (MAA)	78.7	—
Allyl Methacrylate (ALMA)	3.9	—
Methyl-3-Mercaptopropionate (MMP)	13.8	—

55

Rinse DI H₂O

55
601.2

68
2061

5 [Pluronic is a trade mark of ; Alipal is a trade mark of .]

ME #1 Initiator

10

1.0 g of 1.0% Solution of FeSO₄·7H₂O (keep acid with H₂SO₄) in 4 g of DI H₂O.
5.8 g of 70% t-Butyl Hydroperoxide (t-BHP) in 20 g of DI H₂O.
3.6 g of Sodium Sulfoxylate Formaldehyde (SSF) in 40 g of DI H₂O.

15 Neutralizer

16.9 g of Ca(OH)₂ and 36.6 g of 50% NaOH in 123 g of DI H₂O.

ME #2 Initiator

20

6.3 g of Ammonium Persulfate (APS) in 50 g DI H₂O for the kettle charge and 3.1 g of APS in 115 g DI H₂O for a cofeed.

Final Polymer Characterization

25

Percent Solids: 51.0
Particle Size (Brookhaven BI-90): 135 nm
pH: 7.4
Viscosity: 142 cps
Gel: 2.3 g

30

Example 2(c) - 2% ALMA

35

Use same procedure and recipe for example 2(b) except for: 7.9 g of ALMA and 307 g of MMA in ME #1.

Final Polymer Characterization

40

Percent Solids: 50.2
Particle Size (Brookhaven BI-90): 228 nm
pH: 7.4
Viscosity: 640 cps
Gel: 22 g

45

Example 2(d) - 1.5% CMA

50

Use same procedure and recipe for example 2(a) except for: 5.9 g of Crotyl Methacrylate (CMA) and 309 g of MMA in ME #1 in place of the 314.9 g of MMA listed.

Final Polymer Characterization

55

Percent Solids: 48.2
Particle Size (Brookhaven BI-90): 145 nm

EP 0 522 791 B1

pH: 6.9
Viscosity: 75 cps
Gel: 2 g

5 Example 3 - Two-Stage Sequential Core-Shell Polymer Process: Neutralization

Example 3(a) - NH₃

10 Use same procedure and recipe for example 2(b) except for: 5.9 g of ALMA and 309 g of MMA in ME #1, 55 g of NH₃ in 123 g of DI H₂O in the Neutralizer, and add a 1.6 g APS in 25 g of DI H₂O Chaser after the ME #1 exotherm.

Final Polymer Characterization

15 Percent Solids: 49.7
Particle Size (Brookhaven BI-90): 129 nm
pH: 7.5
Viscosity: 160 cps
20 Gel: Trace

Example 3(b) - Ca/Na

25 Use same procedure and recipe for example 2(b) except for: 5.9 g of ALMA and 309 g of MMA in ME #1, 11.8 g of Ca(OH)₂ with 47.5 g of 50% NaOH in 118 g of DI H₂O for the Neutralizer, 1295 g in the kettle to start, and 0.6 g t-BHP/2 g DI H₂O coupled with 0.4 g SSF/4 g DI H₂O to use as a chaser after the ME #1 initiator charge.

Final Polymer Characterization

30 Percent Solids: 45.8
Particle Size (Brookhaven BI-90): 145 nm
pH: 7.5
35 Viscosity: 45 cps
Gel: 0.4 g

Example 3(c) - K/Ca

40 Use same procedure and recipe for example 2(b) except for: 5.9 g of ALMA and 309 g of MMA in ME #1, and 16.9 g of Ca(OH)₂ with 25.6 g of KOH (Potassium Hydroxide) in 170 g of DI H₂O for the Neutralizer, and 900 g of DI H₂O in the kettle to start.

Final Polymer Characterization

45 Percent Solids: 49.8
Particle Size (Brookhaven BI-90): 203 nm
50 pH: 7.2
Viscosity: 45 cps
Gel: 22 g

Example 3(d) - Na/Mg

55 Use same procedure and recipe for example 2(b) except for: 5.9 g of ALMA and 309 g of MMA in ME #1, and 13.3 g of Mg(OH)₂ (Magnesium Hydroxide) with 36.6 g of 50% NaOH in 108 g of DI H₂O for the Neutralizer, and 900 g of DI H₂O in the kettle to start.

Final Polymer Characterization

5 Percent Solids: 50.4
 Particle Size (Brookhaven BI-90): 118 nm
 pH: 7.2
 Viscosity: 170 cps
 Gel: 0.4 g

Example 4 - Two-Stage Sequential Polymerization Process (Other Compositions)Example 4(a)

15 1295 g of DI water was charged to a 5 liter, 4-necked round bottom flask equipped with a mechanical stirrer, condenser and appropriate fittings to produce a nitrogen blanket over the reaction mixture. The kettle contents were then heated to 75°C.

A monomer emulsion (ME #1) was then charged to the kettle followed by an initiator. A few minutes after the temperature levelled off, a chaser was added followed by a neutralizer which solubilized the polymer. Approximately 120 g of ME #2 was added to the kettle followed by an APS initiator charge.

20 The balance of the ME #2 was then gradually added to the same kettle containing the solubilized polymer at a rate so that the reaction temperature stayed in the neighborhood of 80 to 85°C.

The kettle contents were then cooled to 55°C and additional initiator was added to reduce residual monomers to low levels.

Material	ME #1	ME #2
DI H ₂ O	100	395
Pluronic L31 (L31)	37.4	11.8
58% Alipal CO-436	1.4	---
28% Sodium Lauryl Sulfate (SLS)	---	11.2
Butyl Acrylate (BA)	---	799.4
Methyl Methacrylate (MMA)	311	---
Styrene (STY)	---	775.2
Methacrylic Acid (MAA)	78.7	---
Allyl Methacrylate (ALMA)	3.9	---
Methyl-3-Mercaptopropionate (MMP)	13.8	---
Rinse DI H ₂ O	55	68
	<u>601.2</u>	<u>2061</u>

[Pluronic is a trade mark of BASF; Alipal is a trade mark of Rhone-Poulenc]

ME #1 Initiator

45

1.0 g of 1.0% Solution of FeSO₄·7H₂O (keep acid with H₂SO₄) in 4 g of DI H₂O.
 5.8 g of 70% t-Butyl Hydroperoxide (t-BHP) in 20 g of DI H₂O.
 50 3.6 g of Sodium Sulfoxylate Formaldehyde (SSF) in 40 g of DI H₂O.

Neutralizer

55

16.9 g of Ca(OH)₂ and 36.6 g of 50% NaOH in 123 g of DI H₂O.

ME #2 Initiator

6.3 g of Ammonium Persulfate (APS) in 50 g DI H₂O for the kettle charge and 3.1 g of APS in 115 g DI H₂O for a

EP 0 522 791 B1

cofeed.

Final Polymer Characterization

5

Percent Solids: 45.4
Particle Size (Brookhaven BI-90): 159 nm
pH: 7.4
Viscosity: 40 cps
Gel: 0.5 g

10

Example 4(b)

15

Use recipe and procedure as in 4(a) except substitute 992 g of MMA for all of the STY in ME #2, and use 583 g of BA.

Final Polymer Characterization

20

Percent Solids: 46.3
Particle Size (Brookhaven BI-90): 168 nm
pH: 7.1
Viscosity: 45 cps
Gel: 0.1 g

25

Example 4(c)

924 g of DI water was charged to a 5 liter, 4-necked round bottom flask equipped with a mechanical stirrer, condenser and appropriate fittings to produce a nitrogen blanket over the reaction mixture. The kettle contents were then heated to 75°C. A monomer emulsion (ME #1) was then charged to the kettle followed by an initiator. A few minutes after the temperature levelled off, a chaser was added followed by a neutralizer which solubilized the polymer. Approximately 103 g of ME #2 was added to the kettle followed by an APS initiator charge.

30

The balance of the ME #2 was then gradually added to the same kettle containing the solubilized polymer at a rate so that the reaction temperature stayed in the neighborhood of 80 to 85°C.

35

The kettle contents were then cooled to 55°C and additional initiator was added to reduce residual monomers to low levels.

40

Material	ME #1	ME #2
DI H ₂ O	84.6	355
Pluronic L31 (L31)	31.8	10
58% Alipal CO-436	1.2	---
28% Sodium Lauryl Sulfate (SLS)	---	9.6
Butyl Acrylate (BA)	---	669
Methyl Methacrylate (MMA)	258	649
Methacrylic Acid (MAA)	66.9	---
Allyl Methacrylate (ALMA)	5.02	---
50% Acrylamide Solution (AM)	10	40.1
Methyl-3-Mercaptopropionate (MMP)	13.8	---
Rinse DI H ₂ O	---	56
	457.1	1768

45

50

[Pluronic is a trade mark of BASF; Alipal is a trade mark of Rhone-Poulenc]

55

EP 0 522 791 B1

ME #1 Initiator

- 5 9.3 g of a 0.10% solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (keep acid with H_2SO_4).
4.8 g of 70% t-Butyl Hydroperoxide (t-BHP) in 19 g of DI H_2O .
3.1 g of Sodium Sulfoxylate Formaldehyde (SSF) in 35 g of DI H_2O .

Neutralizer

- 10 14.4 g of $\text{Ca}(\text{OH})_2$ and 31.1 g of 50% NaOH in 104 g of DI H_2O .

ME #2 Initiator

- 15 5.35 g of Ammonium Persulfate (APS) in 114 g DI H_2O for the kettle charge and 2.7 g of APS in 104 g DI H_2O for a cofeed.

Final Polymer Characterization

- 20 Percent Solids: 45.1
Particle Size (Brookhaven BI-90): 154 nm
pH: 7.4
25 Viscosity: 34 cps
Gel: 1.2 g

Example 4(d)

- 30 Use recipe and procedure as in 4(a) except substitute STY for MMA in the ME #1 and substitute MMA for STY in ME #2.

Final Polymer Characterization

- 35 Percent Solids: 45.1

Particle Size (Brookhaven BI-90): 199 nm
pH: 8.5
Viscosity: 20 cps
40 Gel: 0.5 g

Example 5 - Blend Polymer Process (Comparative)

- 45 An alkali-soluble polymer similar to polymerizing ME #1 (shell) in example 3(b) was prepared and neutralized. Separately, the ME #2 polymer (core) in the same example was prepared. The two polymers were blended together at a ratio of 1 part of ME #1 polymer solids to 4 parts of ME #2 polymer solids. Yielding the same ratio of shell to core polymer prepared by the in-situ method.

- The ME #2 polymer was prepared by the following method: 1347 g of DI H_2O was charged to a 5 liter, 4-necked round bottom flask equipped with a mechanical stirrer, condenser, and appropriate fittings to produce a nitrogen blanket over the reaction mixture. The kettle contents were then heated to 85°C. A monomer emulsion preform (93 g) was then charged to the kettle followed by an initiator. A few minutes after the temperature levelled off, the balance of the monomer emulsion was then gradually added to the same kettle at a rate so that the reaction temperature stayed in the neighborhood of 80°C to 85°C.

- 55 The kettle contents were then cooled to 55°C and additional initiator was added to reduce residual monomers to low levels.

Material	
DI H ₂ O	556
SLS	24.2
BA	979.2
MMA	949.2
MAA	29.5
Rinse DI H ₂ O	30
	2710.1

Initiator

6.8 g of APS in 30 g DI H₂O.

Example 6 - Two Stage Process Employing Blank Patent Process: Preparation of the Shell (Comparative)

Into a 3 liter, 4-necked round bottom flask, equipped with a mechanical stirrer, condenser and N₂ gas inlet/outlet ports, charge 90 g of propylene glycol and 60 g of 2-ethoxy ethanol. The air in the kettle was displaced with N₂ and the kettle was heated to reflux, i.e., 130° to 135°C. Monomer components were mixed together and then 40 g of Dicumyl Peroxide was mixed in.

The mix was then fed at a rate so that the entire mix would have been added in two hours.

The kettle contents quickly built viscosity and then the reaction was terminated before all the monomer mix was added because it could no longer be stirred.

Monomer Mix	
MMA	1570 g
MAA	400
ALMA	30
MMP	70

The shell (soluble polymer component) could not be made by the Blank Patent method.

Example 7 - Polymer Isolation as a Solid and Use in Portland Cement Modification

A slurry consisting of lime and DI H₂O was mixed into the emulsions so that the final pH was between 8 and 9 and the feed solid content was between 35% and 40%. The neutralized emulsion was then spray-dried using a Bowen Model BLSA laboratory spray dryer. Inlet air temperature was adjusted to 125°C and outlet air temperature was 55°C to 60°C as regulated by the feed rate. Concurrently, a solid anti-caking agent of the type disclosed in US-A-3,985,704 was introduced to the top of the chamber at a rate to yield 5% in the final product. The resulting powders had a residual moisture level of about 2.0% and were free-flowing white powders with average particle size of 50 to 75 microns.

TEST PROCEDURES

(1) Wet-out time - Eighty grams of each of the spray-dried powders prepared above were combined with a dry Portland cement mix consisting of 800 grams of Type I Portland cement, 2000 grams of 60 mesh sand and 8 grams of a solid defoamer (Colloids 775 DD).

Using a Hobart mixer, approximately 370 grams of DI water was mixed into this dry mix until a very workable dough-like consistency was reached. The time required to reach this point was recorded as "wet-out time."

(2) Trowelability - This a subjective test that describes the consistency of the mortar.

(3) Thin section properties - 0.15cm to 0.079cm (1/16 to 1/32 inch) thickness of mortar is placed on the concrete substrate and allowed to cure for 24 hours. Toughness and adhesion of the thin mortar section is tested by using a

knife point and rated qualitatively.

(4) Shearbond adhesion - A 5.08 cm x 5.08 cm x 1.27 cm (2"x2"x0.5" inch) patch of mortar was cast on a concrete block and was cured at room temperature for seven (7) days. The shearbond adhesion strength was calculated by the shearing load required to separate the patch from the concrete divided by the area.

(5) Mortar cure - A 5.08 cm (2-inch) cube mold was filled with mortar. After 24 hours at room temperature, the hardness is rated qualitatively by breaking the mortar cube and scratching the center with a knife.

Application results of the examples 1 through 5 provided in the above are summarized as follows:

Table 1

Modifier Mortar Properties of Powders from Example 1				
Powder	1	2	3	4
Example	1a	1b	1c	1d
Wet out time	30 sec.	30 sec.	30 sec.	30 sec.
Trowelability	excellent	excellent	excellent	excellent
Thin section toughness and adhesion	excellent	excellent	excellent	excellent
5.08 cm (2") Mortar cure (hardness after 24 hrs.)	rock hard	rock hard	rock hard	soft
Shearbond	210 psi	340 psi	370 psi	320 psi
adhesion x 10 ³ Nm ⁻²	1447	2343	2549	2205

Table 2

Modifier Mortar Properties of Powders from Example 2				
Powder	1	2	3	4
Example	Comparative Example 2a	2b	2c	2d
Wet out time	90 sec.	30 sec.	26 sec.	50 sec.
Trowelability	excellent	excellent	excellent	good
Thin section toughness and adhesion	good	excellent	excellent	good
5.08 cm (2") Mortar cure (hardness after 24 hrs.)	soft	rock hard	rock hard	rock hard
Shearbond	150 psi	285 psi	390 psi	200 psi
adhesion x 10 ³ Nm ⁻²	1034	1964	2687	1378

Table 3

Modifier Mortar Properties of Powders from Example 3				
Powder	1	2	3	4
Example	3a	3b	3c	3d
Wet out time	33 sec.	15 sec.	32 sec.	69 sec.
Trowelability	excellent	excellent	excellent	good
Thin section toughness and adhesion	excellent	excellent	excellent	good
5.08 cm (2") Mortar cure (hardness after 24 hrs.)	rock hard	rock hard	rock hard	rock hard
Shearbond	390 psi	470 psi	230 psi	100 psi
adhesion x 10 ³ Nm ⁻²	2687	3238	1584	689

Powders obtained from Example 4(a), 4(b), 4(c) and 4(d) were tested according to the procedures described above. All of the powders were redispersable, and the mortars had excellent trowelability, thin section and bulk cure properties.

EP 0 522 791 B1

Powders made by the process of the present invention, Examples 1(a) - 1(d), 2(b), 2(c), 3(a) - 3(c) and 4(a) - 4(d) were all particularly useful cement modifiers. This was further demonstrated by comparing powders from Example 1 (b) (as a representative) and 5, an acrylic powder DP-1, made by a prior art process (see US-A-4,916,171), a commercially available ethylene-vinyl acetate (EVA) powder and an unmodified mortar.

Table 4

Modifier Mortar Properties					
Powder	1	2	3	4	None
Identification	Example 1b	Example 5	DP-1	EVA	unmodified
Wet out time	25 sec.	64 sec.	150 sec.	15 sec.	---
Trowelability	excellent	good	excellent	good	poor
Thin section toughness and adhesion	excellent	good	excellent	fair	poor
5.08 cm(2") Mortar cure (hardness after 24 hrs.)	rock hard	soft	soft	rock hard	rock hard
Shearbond	340 psi	170 psi	220 psi	200 psi	50 psi
adhesion x 10 ³ Nm ⁻²	2343	1171	1516	1378	344

As illustrated in the above table, powders made from polymers produced by the two-stage sequential polymerization process of this invention showed comparable wet-out time when compared to the commercial product (EVA), 25 seconds versus 15 seconds, but was clearly superior to core-shell polymers, 150 seconds, made from prior art processes, as well as prior art polymer blends, 64 seconds.

Trowelability of the mortar modified with the polymer powder of the present invention was comparable to that of the prior art core-shell polymers but was superior to that of the prior art blends, the commercial product and the unmodified mortar.

Mortar thin section properties were comparable to those of prior art core-shell polymers but clearly superior to those of the prior art blends, the commercial product and the unmodified mortar.

Shearbond adhesion of 2343x10³ Nm⁻² (340 psi) for the mortar modified with the polymer powders of the present invention showed significant improvements over that of the prior art core-shell polymers at 1516x10³ Nm⁻² (220 psi), polymer blends at 1171x10³ Nm⁻² (170 psi), the commercial polymer powder at 1378x10³ Nm⁻² (200 psi), and the unmodified mortar at 344x10³ Nm⁻² (50 psi).

Claims

1. A two-stage aqueous emulsion sequential polymerization method for the preparation of a core-shell polymer, preferably in the form of a powder, comprising:

i. in a first stage

- forming a mixture of monomers comprising from 5 to 40 percent of a carboxylic acid or anhydride, and from 30 to 95 percent of an alkyl acrylate or alkyl methacrylate or styrene, from 0 to 30 percent of a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide,
- polymerizing the mixture in the presence of a polyfunctional compound to form a shell polymer,
- neutralizing the shell with an amine or a base; and

ii. in a second stage,

- forming a mixture of monomers comprising from 70 to 100 percent of an alkyl acrylate or methacrylate or styrene and from 0 to 30 percent of a hydroxyalkyl ester of a carboxylic acid or acrylamide or methacrylamide to produce a calculated Tg of -65 to +35°C;

iii. combining the second-stage monomers mixture with the neutralized polymer of the first stage;

iv. polymerizing the combined monomers of the second stage to form the aqueous emulsion core-shell polymer; and, optionally

v. converting the aqueous emulsion core-shell polymer by spray-drying into a redispersable polymer powder.

2. A method according to claim 1 wherein the weight ratio of the core to the shell is from 95:05 to 60:40, the core having an average molecular weight of greater than 100,000 and the shell having an average molecular weight of 2,500 to 12,000 for the hydrolyzed shell, as determined by gel permeation chromatography.
- 5 3. A method according to claim 1 or claim 2 wherein the T_g of the shell is greater than 60°C, preferably greater than 80°C, and the T_g of the core is from -65 to +35°C, preferably from -40 to +25°C.
4. A method according to any one of the preceding claims wherein the mixture of monomers comprising the shell and the core are selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 10 decyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, butyl methacrylate, acrylonitrile, acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylic anhydride, methacrylic anhydride, maleic anhydride, itaconic anhydride, fumaric anhydride, styrene, substituted styrene, vinyl acetate and other C₁ to C₁₂ alkyl acrylates and methacrylates, acrylamide, methacrylamide, N-methylol methacrylamide, and N-methylol acrylamide.
- 15 5. A method according to claim 4 wherein the mixture of monomers comprising the shell are 5 to 40 percent of a carboxylic acid or anhydride and from 60 to 95 percent of an alkyl acrylate or alkyl methacrylate or styrene, based on the total weight of the shell.
- 20 6. A method according to claim 5 wherein the mixture of monomers comprising the shell are methyl methacrylate, and methacrylic acid.
7. A method according to any one of the preceding claims wherein the mixture of monomers comprising the shell have been neutralized with a base selected from the group consisting of ammonia, triethylamine, monoethanolamine, 25 dimethylaminoethanol, sodium hydroxide and calcium hydroxide and all other Group I A and II A hydroxides.
8. A method according to claim 7 wherein the base is a blend of 30 - 60% calcium hydroxide and 40 - 70% sodium hydroxide, preferably 35 - 50% calcium hydroxide and 50 - 65% sodium hydroxide, based on the total equivalents of acid neutralized.
- 30 9. A method according to claim 7 wherein the base is 100 percent ammonia.
10. A method according to any one of the preceding claims wherein the mixture of monomers comprising the core are 0 to 5 percent of a carboxylic acid or anhydride or acrylamide and from 95 to 100 percent of an alkyl acrylate or 35 alkyl methacrylate or styrene, based on the total weight of the core.
11. A method according to claim 10 wherein the mixture of monomers comprising the core are butyl acrylate and methyl methacrylate.
- 40 12. A method according to claim 10 wherein the mixture of monomers comprising the core are butyl acrylate and styrene.
13. A method according to any one of the preceding claims wherein the polyfunctional compound is selected from the group consisting of polyfunctional compounds having two or more sites of unsaturation, reactive chain transfer agents having two or more abstractable atoms and hybrid polyfunctional compounds having one or more sites of 45 unsaturation and one or more abstractable atoms.
14. A method according to claim 13 wherein the polyfunctional compound is allyl methacrylate.
15. A method according to any one of claims 13 or 14 wherein the polyfunctional compound comprises from less than 50 5 percent, preferably from 0.5 to 3.0 percent based on the total weight of the shell.
16. A core-shell polymer, preferably in the form of a powder, having an alkali-soluble emulsion polymer shell and an aqueous insoluble emulsion polymer core obtainable by a method as defined in any one of the preceding claims.
- 55 17. A polymer according to claim 16 admixed with an effective amount of Portland cement.
18. A method of modifying cementitious compositions comprising admixing an effective amount of Portland cement with an effective amount of the core-shell polymer, preferably in the form of a powder, obtainable or obtained by a method

as defined in any one of claims 1 to 15.

Patentansprüche

5

1. Verfahren für eine zweistufige, sequentielle wäßrige Emulsionspolymerisation zur Herstellung eines Kern/Hülle-Polymers, vorzugsweise in der Form eines Pulvers, umfassend:

i. in einer ersten Stufe

10

- (a) Bilden eines Gemisches von Monomeren, umfassend von 5 bis 40 Prozent einer Carbonsäure oder eines Anhydrids, und von 30 bis 95 Prozent eines Alkylacrylates oder Alkylmethacrylates oder Styrols, von 0 bis 30 Prozent eines Hydroxyalkylesters einer Carbonsäure oder Acrylamids oder Methacrylamids,
- (b) Polymerisieren des Gemisches in der Gegenwart einer polyfunktionellen Verbindung, um ein Hüllepolymer zu bilden,
- (c) Neutralisieren der Hülle mit einem Amin oder einer Base; und
- (d) Bilden eines Gemisches von Monomeren, umfassend von 70 bis 100 Prozent eines Alkylacrylats oder Methacrylats oder Styrols, und von 0 bis 30 Prozent eines Hydroxyalkylesters einer Carbonsäure oder Acrylamids oder Methacrylamids, um eine berechnete Tg von -65 bis +35°C vorzusehen;

20

ii. in einer zweiten Stufe

iii. Vereinigen des Gemisches der Monomeren der zweiten Stufe mit dem neutralisierten Polymer der ersten Stufe;

iv. Polymerisieren der vereinigten Monomeren der zweiten Stufe, um die wäßrige Emulsion des Kern/Hülle-Polymers zu bilden; und, gegebenenfalls,

25

v. Umwandeln des wäßrigen Kern/Hülle-Emulsionspolymers in ein redispersierbares Polymerpulver durch Sprühtrocknen.

30

2. Verfahren gemäß Anspruch 1, wobei das Gewichtsverhältnis des Kerns zur Hülle von 95:05 bis 60:40 ist, wobei der Kern ein mittleres Molekulargewicht von größer als 100.000 und die Hülle ein mittleres Molekulargewicht von 2.500 bis 12.000 für die hydrolysierte Hülle, bestimmt mittels Gelpermeationschromatographie, aufweist.

35

3. Verfahren gemäß Anspruch 1 oder Anspruch 2, wobei die Tg der Hülle größer als 60°C, vorzugsweise größer als 80°C, ist, und die Tg des Kerns von -65 bis +35°C, vorzugsweise von -40 bis +25°C, ist.

40

4. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei das Gemisch der Monomeren, umfassend die Hülle und den Kern, gewählt sind von: Methylacrylat, Ethylacrylat, Butylacrylat, 2-Ethylhexylacrylat, Decylacrylat, Methylmethacrylat, Ethylmethacrylat, Hydroxyethylmethacrylat, Hydroxypropylacrylat, Hydroxypropylmethacrylat, Butylmethacrylat, Acrylnitril, Acrylsäure, Methacrylsäure, Itaconsäure, Maleinsäure, Fumarsäure, Acrylsäureanhydrid, Methacrylsäureanhydrid, Maleinsäureanhydrid, Itaconsäureanhydrid, Fumarsäureanhydrid, Styrol, substituiertes Styrol, Vinylacetat und andere C₁- bis C₁₂-Alkylacrylate und -methacrylate, Acrylamid, Methacrylamid, N-Methylolmethacrylamid und N-Methylolacrylamid.

45

5. Verfahren gemäß Anspruch 4, wobei das Gemisch der Monomeren, welche die Hülle umfassen, 5 bis 40 Prozent einer Carbonsäure oder eines Anhydrids und von 60 bis 95 Prozent eines Alkylacrylates oder Alkylmethacrylates oder Styrols, bezogen auf das Gesamtgewicht der Hülle, ist.

50

6. Verfahren gemäß Anspruch 5, wobei das Gemisch der Monomeren, welche die Hülle umfassen, Methylmethacrylat und Methacrylsäure sind.

55

7. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei das Gemisch der Monomeren, welche die Hülle umfassen, mit einer Base neutralisiert worden ist, die aus Ammoniak, Triethylamin, Monoethanolamin, Dimethylaminoethanol, Natriumhydroxid und Kalziumhydroxid und allen anderen Hydroxide der Gruppen IA und IIA gewählt ist.

8. Verfahren gemäß Anspruch 7, wobei die Base eine Mischung aus 30-60% Calciumhydroxid und 40-70% Natriumhydroxid, vorzugsweise 35-50% Calciumhydroxid und 50-65% Natriumhydroxid, bezogen auf die Gesamtäquivalente neutralisierter Säure, ist.

EP 0 522 791 B1

9. Verfahren gemäß Anspruch 7, wobei die Base 100 Prozent Ammoniak ist.
10. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei das Gemisch der Monomeren, welche den Kern umfassen, 0 bis 5 Prozent einer Carbonsäure oder eines Anhydrids oder Acrylamids und von 95 bis 100 Prozent eines Alkylacrylates oder Alkylmethacrylates oder Styrols, bezogen auf das Gesamtgewicht des Kerns, ist.
11. Verfahren gemäß Anspruch 10, wobei das Gemisch der Monomeren, welche den Kern umfassen, Butylacrylat und Methylmethacrylat sind.
12. Verfahren gemäß Anspruch 10, wobei das Gemisch der Monomeren, welche den Kern umfassen, Butylacrylat und Styrol sind.
13. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die polyfunktionelle Verbindung aus polyfunktionellen Verbindungen mit zwei oder mehreren ungesättigten Stellen, reaktiven Kettenübertragungsmitteln mit zwei oder mehreren entfernbaren Atomen, und polyfunktionellen Hybridverbindungen mit einer oder mehreren ungesättigten Stellen und einem oder mehreren entfernbaren Atomen gewählt ist.
14. Verfahren gemäß Anspruch 13, wobei die polyfunktionelle Verbindung Allylmethacrylat ist.
15. Verfahren gemäß einem der Ansprüche 13 oder 14, wobei die polyfunktionelle Verbindung weniger als 5 Prozent, vorzugsweise von 0,5 bis 3,0 Prozent, bezogen auf das Gesamtgewicht der Hülle, umfaßt.
16. Kern/Hülle-Polymer, vorzugsweise in der Form eines Pulvers, mit einer alkalilöslichen Emulsionspolymerhülle und einem wäßrigen, unlöslichen Emulsionspolymerkern, erhältlich nach einem Verfahren, wie in einem der vorhergehenden Ansprüche definiert.
17. Polymer gemäß Anspruch 16, gemischt mit einer wirksamen Menge Portlandzement.
18. Verfahren zum Modifizieren zementartiger Zusammensetzungen, umfassend ein Mischen einer wirksamen Menge Portlandzement mit einer wirksamen Menge des Kern/Hülle-Polymers, vorzugsweise in der Form eines Pulvers, erhältlich oder erhalten nach einem Verfahren, wie in einem der Ansprüche 1 bis 15 definiert.

Revendications

1. Procédé de polymérisation séquentielle en émulsion aqueuse, à deux étapes, pour la préparation d'un polymère à noyau et enveloppe, de préférence sous forme de poudre, comprenant:
- i. dans une première étape
- (a) former un mélange de monomères comprenant de 5 à 40% d'un acide ou anhydride carboxylique et de 30 à 95% d'un acrylate d'alkyle ou méthacrylate d'alkyle ou styrène, de 0 à 30% d'un ester hydroxyalkylique d'un acide carboxylique ou acrylamide ou méthacrylamide,
- (b) polymériser le mélange en présence d'un composé polyfonctionnel pour former un polymère d'enveloppe,
- (c) neutraliser l'enveloppe avec une amine ou une base; et
- ii. dans une seconde étape,
- (d) former un mélange de monomères comprenant de 70 à 100% d'un acrylate ou méthacrylate d'alkyle ou d'un styrène et de 0 à 30% d'un ester hydroxyalkylique d'un acide carboxylique ou acrylamide ou méthacrylamide pour produire une Tg calculée de -65 à +35°C;
- iii. combiner le mélange de monomères de la seconde étape avec le polymère neutralisé de la première étape;
- iv. polymériser les monomères combinés de la seconde étape pour former le polymère à noyau et enveloppe en émulsion aqueuse; et, le cas échéant,
- v. convertir le polymère à noyau et enveloppe en émulsion aqueuse, par séchage par atomisation, en une poudre de polymère redispersable.

2. Procédé selon la revendication 1, dans lequel le rapport pondéral du noyau à l'enveloppe est de 95:05 à 60:40, le noyau ayant une masse moléculaire moyenne supérieure à 100 000 et l'enveloppe ayant une masse moléculaire moyenne de 2 500 à 12 000 pour l'enveloppe hydrolysée, les déterminations étant faites par chromatographie par perméation de gel.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel la T_g de l'enveloppe est supérieure à 60°C, de préférence supérieure à 80°C, et la T_g du noyau est de -65 à +35°C, de préférence de -40 à +25°C.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel les mélanges de monomères constituant l'enveloppe et le noyau sont choisis dans le groupe constitué par l'acrylate de méthyle, l'acrylate d'éthyle, l'acrylate de butyle, l'acrylate de 2-éthylhexyle, l'acrylate de décyle, le méthacrylate de méthyle, le méthacrylate d'éthyle, le méthacrylate d'hydroxyéthyle, l'acrylate d'hydroxypropyle, le méthacrylate d'hydroxypropyle, le méthacrylate de butyle, l'acrylonitrile, l'acide acrylique, l'acide méthacrylique, l'acide itaconique, l'acide maléique, l'acide fumarique, l'anhydride acrylique, l'anhydride méthacrylique, l'anhydride maléique, l'anhydride itaconique, l'anhydride fumarique, le styrène, le styrène substitué, l'acétate de vinyle, et d'autres acrylates et méthacrylates d'alkyle en C_1-C_{12} , l'acrylamide, le méthacrylamide, le N-méthylolméthacrylamide et le N-méthylolacrylamide.
5. Procédé selon la revendication 4, dans lequel le mélange de monomères constituant l'enveloppe comprend de 5 à 40% d'un acide ou anhydride carboxylique et de 60 à 95% d'un acrylate d'alkyle ou méthacrylate d'alkyle ou styrène, par rapport au poids total de l'enveloppe.
6. Procédé selon la revendication 5, dans lequel le mélange de monomères constituant l'enveloppe est constitué de méthacrylate de méthyle et d'acide méthacrylique.
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange de monomères constituant l'enveloppe a été neutralisé avec une base choisie dans le groupe constitué par l'ammoniac, la triéthylamine, la monoéthanolamine, le diméthylaminoéthanol, l'hydroxyde de sodium et l'hydroxyde de calcium, et tous les autres hydroxydes des groupes IA et IIA.
8. Procédé selon la revendication 7, dans lequel la base est un mélange de 30-60% d'hydroxyde de calcium et de 40-70% d'hydroxyde de sodium, de préférence de 35-50% d'hydroxyde de calcium et de 50-65% d'hydroxyde de sodium, par rapport au total des équivalents d'acide neutralisé.
9. Procédé selon la revendication 7, dans lequel la base est 100% d'ammoniac.
10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange de monomères constituant le noyau comprend 0 à 5% d'un acide ou anhydride carboxylique ou d'acrylamide et de 95 à 100% d'un acrylate d'alkyle ou méthacrylate d'alkyle ou styrène, par rapport au poids total du noyau.
11. Procédé selon la revendication 10, dans lequel le mélange de monomères constituant le noyau est constitué d'acrylate de butyle et de méthacrylate de méthyle.
12. Procédé selon la revendication 10, dans lequel le mélange de monomères constituant le noyau est constitué d'acrylate de butyle et de styrène.
13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé polyfonctionnel est choisi dans le groupe constitué par les composés polyfonctionnels portant deux sites d'insaturation ou plus, les agents de transfert de chaîne réactifs possédant deux atomes extractibles ou plus, et les composés polyfonctionnels hybrides portant un ou plusieurs sites d'insaturation et un ou plusieurs atomes extractibles.
14. Procédé selon la revendication 13, dans lequel le composé polyfonctionnel est le méthacrylate d'allyle.
15. Procédé selon l'une quelconque des revendications 13 ou 14, dans lequel le composé polyfonctionnel constitue moins de 5%, de préférence de 0,5 à 3,0%, du poids total de l'enveloppe.
16. Polymère à noyau et enveloppe, de préférence sous forme de poudre, possédant une enveloppe de polymère en émulsion soluble dans les bases et un noyau de polymère en émulsion insoluble dans les milieux aqueux, pouvant être obtenu par un procédé tel que défini dans l'une quelconque des revendications précédentes.

EP 0 522 791 B1

17. Polymère selon la revendication 16, mélangé avec une quantité efficace de ciment Portland.

18. Procédé pour modifier des compositions de ciment comprenant le mélange d'une quantité efficace de ciment Portland avec une quantité efficace du polymère à noyau et enveloppe, de préférence sous forme de poudre, pouvant être obtenu par un procédé tel que défini dans l'une quelconque des revendications 1 à 15.

10

15

20

25

30

35

40

45

50

55